

## Removal of Azo Compounds from Aqueous Solutions by the Process of Adsorption on Bentonite Surfaces

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(Received on: April 7, 2013)

### ABSTRACT

The preparations of azo compounds and adsorption of azo compounds on Bentonite surface was investigated by UV-Visible spectrophotometric Technique, The isotherms were of type S4 according to Giles Classification. The effect of contact time was investigated and found that the adsorption process on Bentonite was reached complete equilibrium within 30 min. The effect of weight was investigated for 0.01- 0.2g. Adsorption on Bentonite surface was examined as a function of temperature in the range (303-333K). The extent of adsorption was found to decrease with the increase in temperature (Exothermic). The thermodynamic function  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  were calculated. The Freundlich and Langmuir isotherm equations were applied to the data and values of parameter of these isotherm equation were evaluated the adsorption. The effect of initial pH on adsorption capacity between (2-14).

**Keywords:** Adsorption, azo compounds, Freundlich, Langmuir, Isotherms.

### INTRODUCTION

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. They are highly colored and have been used as azo compounds and pigments for a long time, Nowadays, synthetic azo compounds

are widely used in different application fields, such as medicines, cosmetics, food, paints, plastics, shipbuilding, automobile industry, cable manufacture, etc<sup>1-12</sup>. However, the traditional application field of the synthetic azo compounds still remains the textile industry, and the finishing of fibrous materials in order to impart

simultaneously with coloration, antimicrobial properties is of great interest. Today's experiments deal with a class of compounds called azo compounds, compounds that contain two aromatic fragments connected by a N=N double bond. You may have encountered these in chemistry experiments as they are typical pH indicators. They are straightforward to make and of industrial importance. Azo compounds are prepared in a two step reaction, the first being the synthesis of an aromatic diazonium ion from an aniline derivative. The next step is coupling of the diazonium salt with an aromatic compound A,B. The colours of azo compounds include different shades of yellow, red, orange, brown, and blue. Each group is assigned a different coupling reaction and all of the azo compounds synthesized will be compared at the end of the lab session.

Personal protective equipment including safety goggles, gloves and a lab coat must be worn at all times during the experiment. Long pants should be worn along with close-toed shoes. No food or drink is allowed in the lab. Always work in the fume hood. Be careful when handling the products, they are deeply coloured and will stain your skin and cloth for a long period of time. Do not wipe gloves on lab coats<sup>(13)</sup>. Rapid progress in industrial activities during recent years has led to the discharge of unprecedented amount of wastewater containing synthetic azo compounds, which pollutes the rivers and consequently causes harm to human and other living organisms. A majority of the used azo compounds are azo reactive azo compounds<sup>(14)</sup>. These are bright color azo compounds due to the presence of one or several azo (-N = N-)

groups associated with substituted aromatic structures<sup>15</sup>. Effluents from textile, leather, food processing, cosmetics, paper and dye manufacturing industries are some examples of the sources of discharged azo compounds<sup>16</sup>. These azo compounds or their breakdown products are toxic to living organisms<sup>17</sup>. The above reasons have prompted enormous research interest in the use of agricultural waste as starting materials because of their low-cost and widespread availability. Some examples of agro waste that have been used for the removal of azo compounds are palm kernel fibers<sup>18</sup>, coir pith<sup>19</sup>, sugarcane bagasse<sup>20</sup>, banana peel<sup>21</sup>, peanut hull<sup>22</sup>, rice bran and wheat bran<sup>23</sup>, rice husk<sup>24</sup>, tea waste<sup>25</sup>, waste apricot<sup>26</sup>, rubber seed coat<sup>27</sup>, coconut shell<sup>28</sup>, apple pomace and wheat straw<sup>29</sup>, halzelnut shell<sup>30</sup>, plum kernel<sup>31</sup>, corncob and barley husk<sup>32</sup>, bamboo<sup>33</sup>, grass waste<sup>34</sup>, pumpkin seed hull<sup>35</sup> and garlic peel<sup>36</sup>.

The present study is focused on the possibility of developing new eco friendly azo compounds with good colouristic and application properties, and exhibiting biological activity.

## EXPERIMENTAL PART

### MATERIALS AND METHODS

#### Synthesis of the azo compounds

The preparation of compounds A,B is shown below. The structure of these compounds was confirmed by FT-IR, <sup>1</sup>H-NMR mass spectrum.

#### -Synthesis of compound (A)

This compound prepared from solving 4-amino antipyrine with acetyl acetone by two steps:

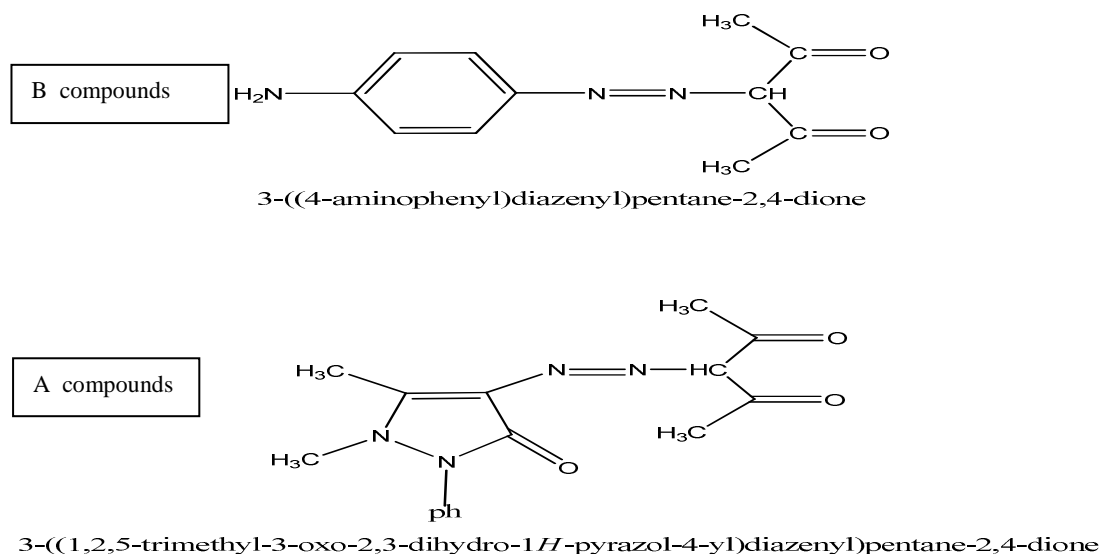
The first step includes solving 4-amino antipyrine (1.5 gm , 0.001 mole) in hydrochloric acid (10 ml) with (20ml) of distilled water and (0.69 gm,0,012 mole) of sodium nitrite that solved in (10 ml) distilled water, was add and maintained at temperature not above (0-5) C°( ice - bath) to form Diazoinum salt. The second step includes coupling reactions between the product compound with one mole from acetyl acetone (1.5ml, 0.015 mole) solved in 30 ml absolute ethanol and (1 ml) from sodium hydroxide( %10), the melting point of A compound 184-182°C and molecular weight 314(C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>) and R<sub>f</sub> =0.68. Fig .1 .

#### - Synthesis of compound (B)

This compound prepared from solving

p- phenylene diamine with acetyl cetone by two steps:

The first step includes solving p-phenylene di amine (1.5 gm , 0.006 mole) in hydrochloric acid (10 ml) with (20ml) of distilled water and (0.69 gm,0,012 mole) of sodium nitrite that solved in (10 ml) distilled water ,was add and maintained at temperature not above (0-5) C°( ice - bath) to form Diazoinum salt. The second step includes coupling reactions between the product compound with one mole from acetyl acetone (1.5ml, 0.015 mole) solved in 30 ml absolute ethanol and (1 ml) from sodium hydroxide ( % 10 ) the melting point of A compound 146-144°C and molecular weight 219(C<sub>11</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>) and R<sub>f</sub> =0.59 Fig.1 in shown below:



Figure(1): Synthesis of the azo compounds

#### Preparation of azo compounds solutions

Standard stock solution of 200ppm of azo compounds was prepared by

dissolving 0.02g of azo compounds in a minimum amount of distilled water in a 100ml volumetric flask and volume were made up to the mark with distilled water.

The Solution of different concentration were prepared by serial dilutions for azo compounds between 2-20ppm. The calibration curves in the concentration range that falls in the region of applicability of Bear-Lambert's law were employed.

### Preparation of clay powder

The clay was washed with excessive amounts of distilled water, it was suspended in HCl solution pH=3 to remove carbonate and it was washed with an excess amount of distilled water to remove the soluble materials<sup>(37)</sup>. And it was dried at 150°C for three hours. The clay was ground and sieved to a particle size of 600µm.

### Methods

To determine the equilibrium time that is needed for the adsorption system to reach equilibrium at a given temperature, the following procedure was the concentration of 20ppm for azo compounds put in 15ml of azo compounds glass bottles that was shaken with 0.2gm from the Bentoinate, that the concentration of adsorbate solution was determined spectrophotometry at different times 15- 210min, until the equilibrium time of adsorption. The effect of pH is by the range (2-14) and the effect of initial concentration.

The quantities of azo compounds adsorbed were calculated according to the following equation<sup>38</sup>.

$$Q_e = (C_o - C_e) V / m$$

$Q_e$  : is the amount of azo compounds adsorbed (mg/g)

$C_o$  and  $C_e$  : are the initial and equilibrium concentrations (ppm) of the adsorbate in solution, respectively,

$V$  : is the volume of solution (L) and ( $m$ ) is the mass of adsorbent(g).

## RESULTS AND DISCUSSION

### Spectroscopic study

Fourier Transform Infrared (FTIR) was used to identify the characteristic functional groups in the A, B compounds. A known quantity (5 mg) of the A,B compounds sample was powdered and then dispersed in dry potassium bromide (KBr). The mixture was thoroughly mixed in a mortar and pressed at pressure of 6 bars within 2 min to form a KBr thin disc. Then the disc was placed in a sample cup of a diffuse reflectance accessory. The IR spectrum was obtained using Perkin Elmer 2000 infrared spectrometer. The sample was scanned from 4000-400  $\text{cm}^{-1}$  for 16 times to increase the signal to noise ratio. The aim of using FTIR analysis is to determine the existence of functional groups that exists on A,B compounds is shown in Fig. 2,3. The synthesized compound (A) : The FT-IR spectrum of (A) compound  $\square(\text{cm}^{-1})$  showed bands at: 1680 ( $\text{C}=\text{O}$ , ketone), 1653 ( $\text{N}=\text{N}$ , azo), 1519 ( $\text{C}=\text{C}$ , aromatic), 2941 ( $\text{C}_\text{H}$ , alephatic), 2999 ( $\text{C}_\text{H}$ , aromatic).

The synthesized compound (B): The FT-IR spectrum of (B) compound  $\square(\text{cm}^{-1})$  showed bands at : 1670 ( $\text{C}=\text{O}$ , ketone), 1627 ( $\text{N}=\text{N}$ , azo), 1500 ( $\text{C}=\text{C}$ , aromatic), 3462 ( $-\text{NH}_2$  group), 3055 ( $\text{C}_\text{H}$ , aromatic), 2924 ( $\text{C}_\text{H}$ , aliphatic).

In this study was used to identify the signal in the A,B compounds The H1- NMR spectrum of compound (A) : 1.68  $\delta$  (S,3H,CH<sub>3</sub>) ; 3.01  $\delta$  (S,1H,C<sub>H</sub>) ; (7.2-7.0)  $\delta$  (S,3H,Ar-H). The H1- NMR spectrum of

compound (B) : 1.43  $\delta$  (S,3H,CH<sub>3</sub>) ; 2.92  $\delta$  (S,1H,C-H) ; (7.2-6.7)  $\delta$  (d,3H,Ar-H) ; 9.96  $\delta$  (S,2H,NH<sub>2</sub>) Fig.4,5 .

### Effect of Contact time

The relationship between contact time and adsorption capacity of azo compounds by the Bentonite was conducted through batch experiments to achieve the equilibrium as shown in Fig .6 .The results showed that the equilibrium time was reached within 120 min of operation .The adsorption capacity was constant thereafter for case of all compounds observed .The compounds was found to be more effective for Bentonite compared to the A and B compounds.

### Effect of adsorbent dose

The effect of sorbent dose on the equilibrium uptake of azo compounds was investigated with sorbent masses of 0.01, 0.05 ,0.1 ,0.15 and 0.2 g .The experiments were performed by adding the known weights of Bentonite to ten conical flask 50 ml containing 15ml of 0.1g solution at pH=7.The flasks were shaken at 200rpm and 303k for 120min and equilibrium concentration of the remaining compounds was determined spectrophotometrically (Fig.7) .

### Adsorption isotherms

Adsorption isotherms are important for the description of how adsorbates will interact with an adsorbent and are critical in optimizing the use of adsorbent .Thus ,the correlation of equilibrium data using either a theoretical or empirical equation is essential

for adsorption data interpretation and prediction .Several mathematical models can be used to describe experimental data of adsorption isotherms (Fig.8) .two famous isotherms equation, the Langmuir, Freundlich isotherms are applied in this study .

### Adsorbents Freundlich isotherm Langmuir isotherm

It is generally possible to express the results of experimental sorption measurements in the form of equilibrium sorption isotherms. In this, two types of isotherms have been investigated, namely the Langmuir and Freundlich isotherms. The Langmuir equation assumes that there is no interaction between the sorbet molecules and that the sorption is localized in a monolayer (Fig.9). It is then assumed that once a compounds molecule occupies a site, no further sorption on take place at this site. Theoretically, therefore, a saturation value is reached, beyond which no further sorption can take place. The Freundlich equation is an empirical relationship describing the sorption of solutes from a liquid to a solid surface Fig.(10). The equations for the two types of sorption isotherms are given by<sup>39</sup>.

Langmuir isotherm  $C_e / Q_e = 1/a_b + (1/a) C_e$   
Freundlich isotherm  $\log Q_e = \log K_f + 1/n \log C_e$

Where  $C_e$  is the equilibrium concentration of compounds in solution (mg/L),  $Q_e$  is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of sites (mg/g), (a) is a constant related to the area occupied by monolayer of sorbet, reflecting the sorption capacity (mg/g), (b) is a dried measure for

the intensity of the sorption process ( $L/mg$ ), ( $K$ ) represents the quantity of compounds adsorbed in ( $mg/g$ ) adsorbent for a unit equilibrium concentration of the compound under test. In order to decide which type of isotherms fits better the sorption experimental data, we plotted the quantities  $\log Q_e$  Vs  $\log C_e$  for the Freundlich isotherm and  $C_e/Q_e$  Vs  $C_e$  for the Langmuir isotherm. The  $R^2$  values computed by linear regression for the two types of isotherms are presented in table (1) for the two serpents.

### Effect of pH

The influence of pH for the adsorption of compounds were observed (Fig.11). For this purpose experiments at different pH for each compounds were accomplished 15ml solution of compounds carrying variable pH (2-14) was added in different solutions HCl, NaOH with optimum of weight surface in experimental. The initial pH values of the dye solution affect the surface charge of the adsorbent and thus the adsorption of the charged dye groups on it, we can observe the maximum adsorption occurred at pH =3.0 for B compounds and pH=6.0 for A compounds because the overall surface charge on the adsorbent became negative and the high attractive forces will be occurred between the azo compounds molecules and the surface

### Temperature Effect and Thermodynamic Parameters

The adsorption of compounds on Bentonite at four different temperatures has been carried out. Variable temperature study will help in evaluating the basic

thermodynamical functions. ( $\Delta H, \Delta S, \Delta G$ ) of the adsorption processes A, B compounds adsorption decreases with increasing temperature, showing the exothermic nature of the process. The general shapes of the compounds adsorption on the Bentonite are given in (Fig.12).

Thermodynamic parameters were evaluated to confirm the adsorption nature of the present study. The thermodynamic constants, free energy change ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process, Based on the following literature available equations. The plot of  $\ln K_c$  versus  $1/T$  (Fig.13) Table(2) given a straight line from which  $\Delta H$ ,  $\Delta S$  can be calculated from the slope and intercept.

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\Delta G = -RT \ln k_c$$

Where:  $R$ : is the ideal gas constant (8.314 J/mol.k),  $T$ : is the absolute temperature  
 $K_c$ : is the equilibrium constant for the adsorption process at each temperature  $C_{ad}$  and  $C_{eq}$  are the concentrations of azo compounds on the Bentonite and at equilibrium respectively. The negative  $\Delta H$  values indicates the exothermic nature of compounds adsorption onto Bentonite. The positive  $\Delta G$  values confirm the nonspontaneous nature of adsorption process even with positive  $\Delta G$  values and The negative  $\Delta G$  values confirm the spontaneous nature of adsorption process, there is some sort of interactions but weak interactions<sup>40</sup>. By increasing concentration of the reactants, it may often be possible to make the reaction

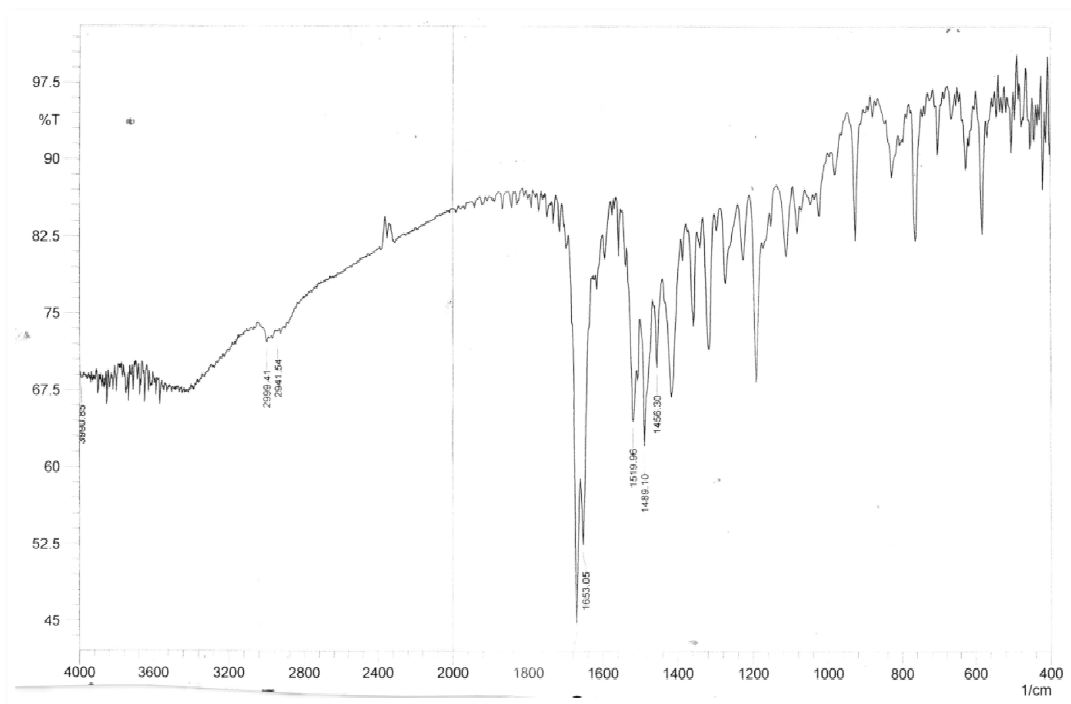
to proceed even if  $\Delta G$  has a positive value. This is the normal consequence of the physical adsorption phenomenon, which takes phase through electrostatic interactions<sup>4</sup>. The negative  $\Delta S$  values suggest the decrease in adsorbate concentration in solid – solution interface indicating thereby the increase in sorbate concentration onto the solid phase.

**Table.1 The Langmuir, Freundlich constants for the adsorption of azo compounds Bentoniate**

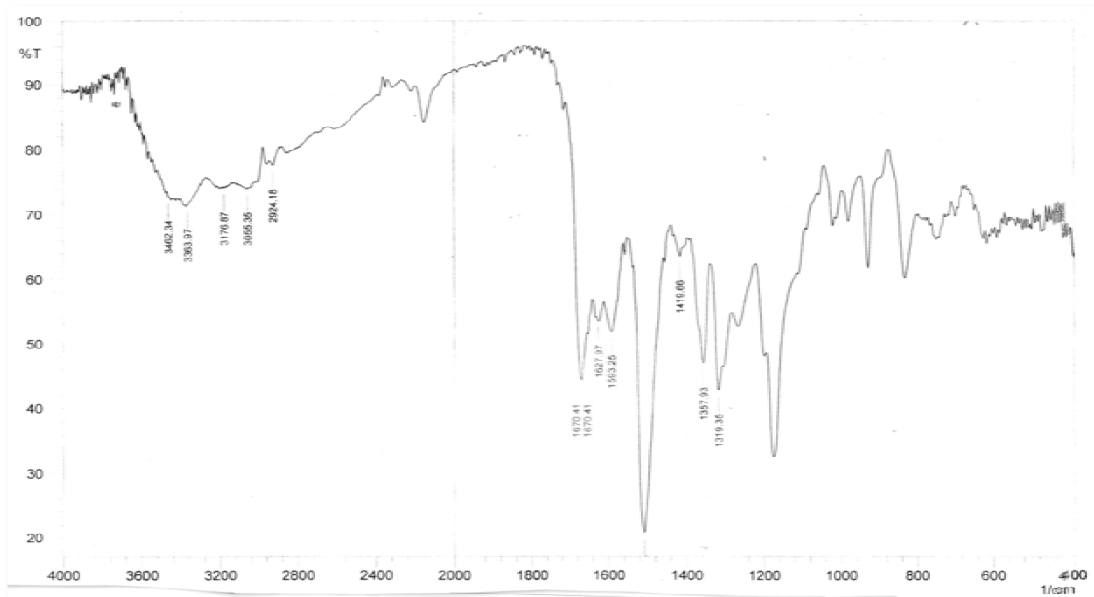
Dyes	$K_f$	n	$R^2$	a	b	$R^2$
A compounds		2.08	0.962	0.79	1.12	0.972
B compounds	1.78	1.22	0.968	3.57	2.22	0.691

**Table.4 Thermodynamic parameters for the adsorption of azo compounds onto Bentoniate**

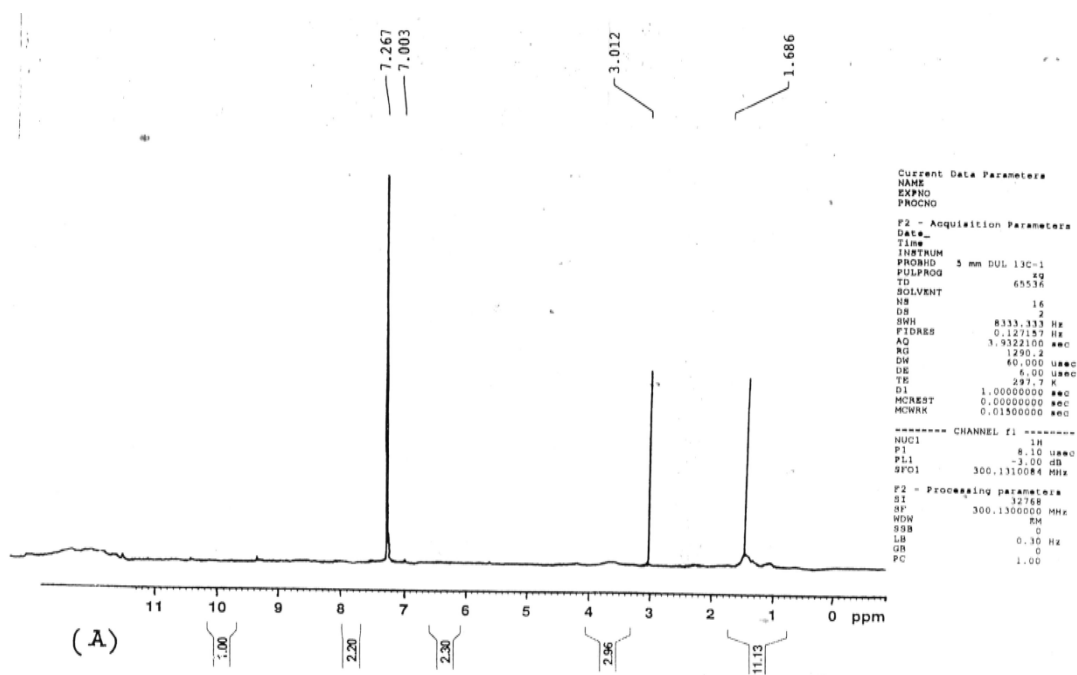
Dyes	$-\Delta H(\text{KJ.mol}^{-1})$	$\Delta G(\text{KJ.mol}^{-1}.\text{k}^{-1})$	$\Delta S(\text{J.mol}^{-1})$ -
A compounds	6.96	4.853-	95.86
B compounds	6.66	3.566	66.39



**Figure(2): FTIR spectra of A compound at room temperature**



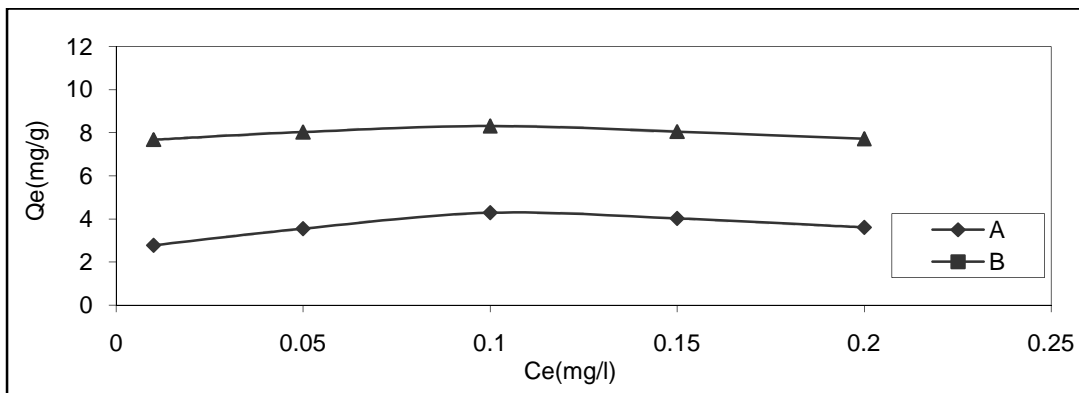
Figure(3):FTIR spectra of B compounds at room temperature



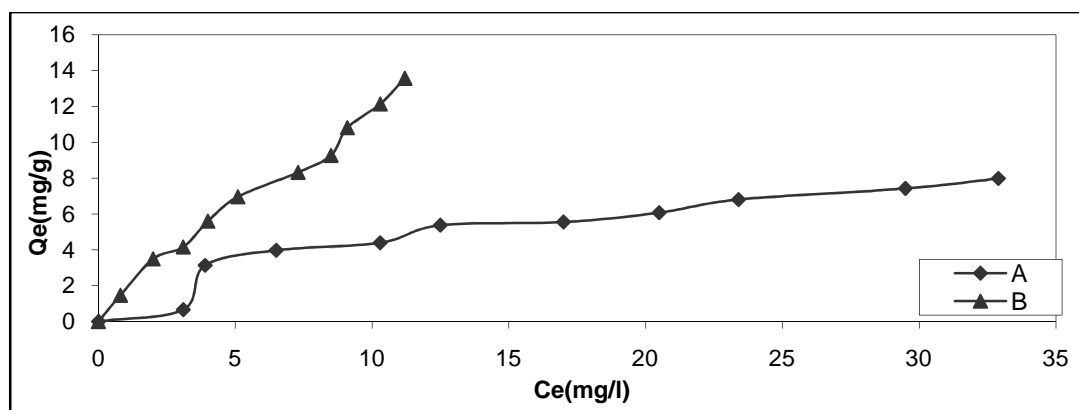
Figure(4): H1- NMR spectra of A compound at room temperature







Figure(7) Effect of weight adsorbent for compounds on Bentonite



Figure(8):Isotherms adsorption for compounds on Bentonite

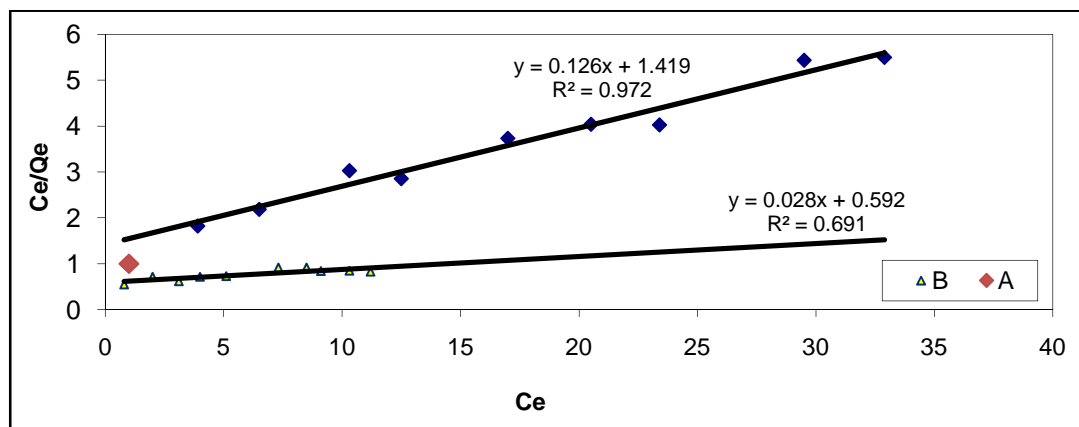


Figure (9):Langmuir adsorption isotherms for compounds on Bentonite

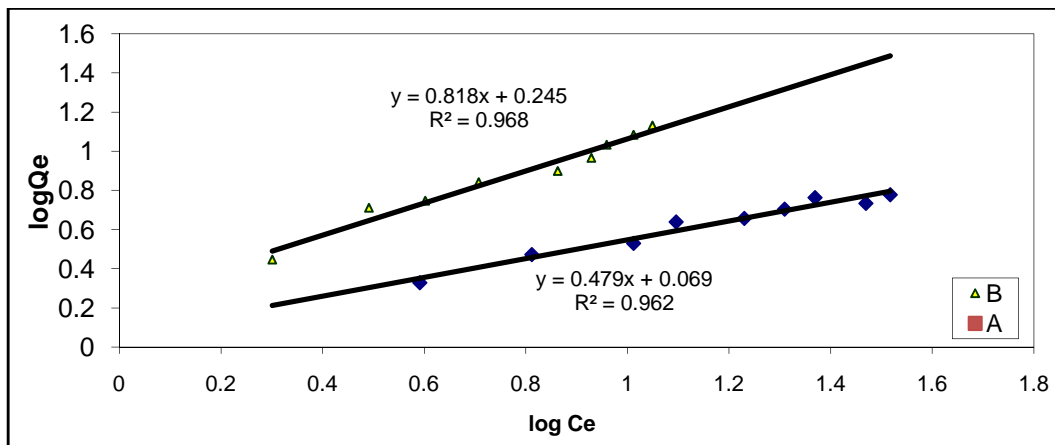
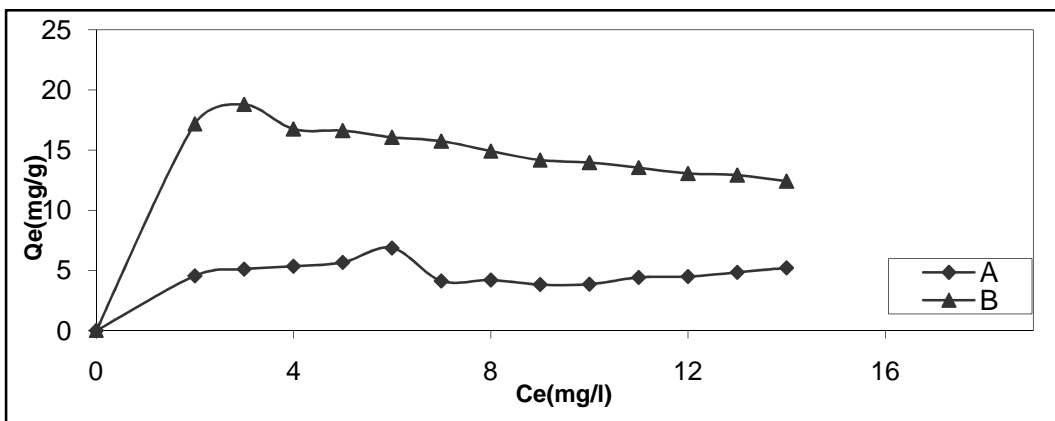
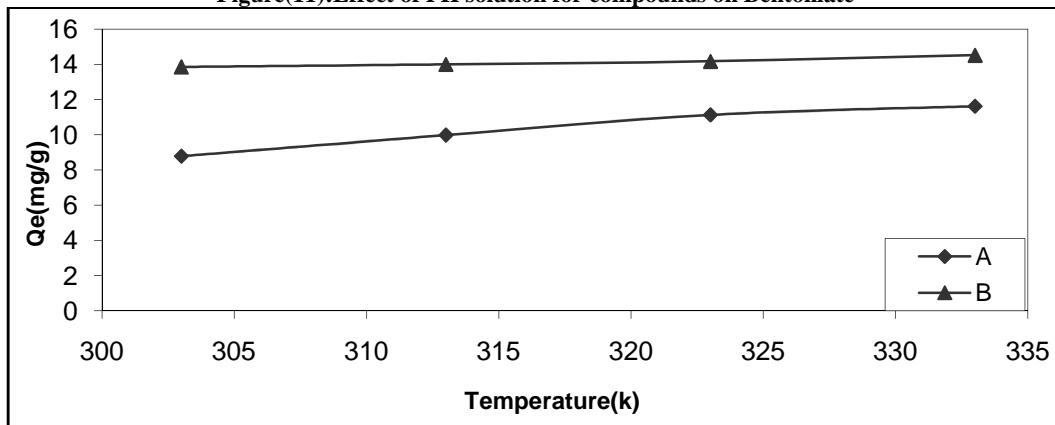


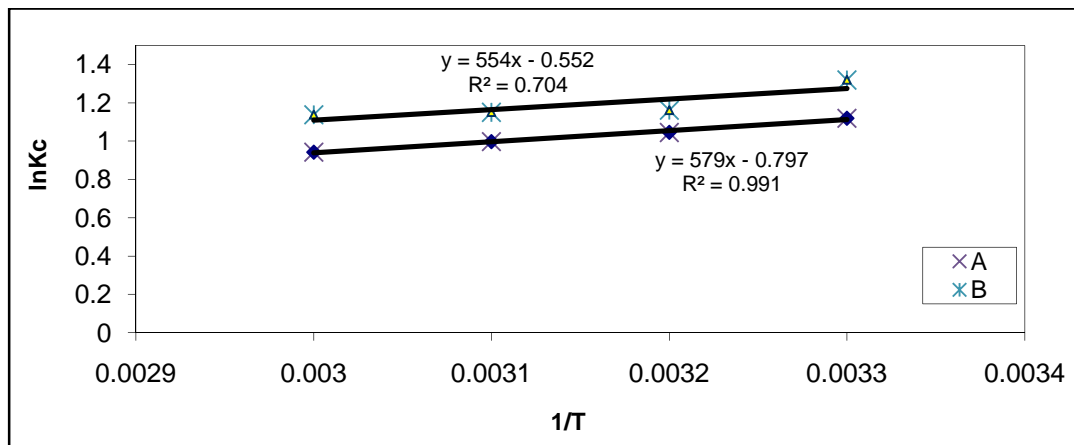
Figure (10): Freundlich adsorption isotherms for compounds on Bentonite



Figure(11): Effect of PH solution for compounds on Bentonite



Figure(12): Effect of temperature for compounds asorption on Bentonite



Figure(13):relation between ln Kc and 1/T for compounds on Bentonite

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